

ON THE MECHANISM OF GAS HYDRATE FORMATION IN SUBSEA SEDIMENTS

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INTRODUCTION

Gas hydrates are crystalline molecular complexes formed from mixtures of water and suitably sized gas molecules. Based on hydrogen bonding, water molecules form unstable lattice structures with several interstitial cavities. The gas molecules can occupy the lattice cavities and, when a minimum number of cavities are occupied, the crystalline structure becomes stable and solid gas hydrates are formed, even at temperatures well above the ice point^[1]. The known gas hydrate structures are; structure-I, structure-II, and the recently discovered structure-H^[2].

The necessary condition for hydrate formation is the presence of water or ice, suitably sized non-polar or slightly polar molecules, together with appropriate pressure and temperature conditions. In subsea environments, the sediments are normally saturated with sea water and a combination of the geothermal gradient and the weight of the column of water (which causes a hydrostatic pressure) could provide the right conditions for hydrate formation. Under these conditions, gas released from biogenic activities (or seepage from oil and gas reservoirs) could form gas hydrates. Current estimates show that the amount of energy in the gas hydrates is twice that of the total fossil fuel reserves, indicating a huge source of energy which could be exploited in the right economical conditions^[1].

Although most scientists agree on the process of hydrate formation in subsea sediments, the mechanism of gas hydrate formation is the subject of some debate. Some researchers suggest that the presence of the free gas phase is necessary and gas hydrates form in the gas-water interface. Others believe that at least a local supersaturation of gas with respect to gas-water equilibria is required. Some propose that this supersaturation will result in the evolution of micro-bubbles and hence formation of gas hydrates. While others suggest that there is no need for the presence of gas bubbles for the hydrates to be stable^[1,3-5].

In this presentation, a thermodynamic model, validated against experimental data, is used to predict the solubility of methane in pure or saline water. The results show that gas hydrates could form from dissolved gas as well as from free gas. Based on the above findings, two mechanisms for hydrate formation in subsea sediments have been suggested and discussed.

It should be noted that, the hydrate forming gas is assumed to be pure methane to simplify the argument. Obviously for multi-component systems, upon hydrate formation, some compositional variation will occur which will result in changes in equilibrium conditions. Also, any effect due to capillary forces and the type of rock has been ignored in this work.

THERMODYNAMIC MODEL

The fugacity of each component in all fluid phases, including the salt free water-rich phase, have been calculated by an equation of state (EoS). The saline water phase has been modelled by combining the EoS with the modified Debye-Hückel electrostatic term, using only one interaction parameter. In optimising the water-salt interaction parameters, water vapour pressure depression data at 373.15 K and freezing point depression data have been used. For the gas-salt interaction coefficient, gas solubility data in single electrolyte solutions at different temperatures and salt concentrations have been used. The model has been extended to mixed electrolyte solutions with nine salts in its library. A detailed

description of modelling vapour, liquid hydrocarbon, salt free water phase, hydrate phases, ice phase, and saline water phase is given elsewhere[6, 7].

Figure-1 shows methane solubility in distilled water at different temperatures. There is a good agreement between experimental[8] data and predictions which demonstrates the success of the EoS in representing highly polar systems.

Methane solubility in distilled water and in 1 and 4 molar NaCl solutions are presented in Figure-2. The agreement between experimental[9] data and predictions is very good, which indicates the reliability of the thermodynamic model. (There are some deviations for pure water at higher pressures, which could be due to the inaccuracy of experimental data, as Figure-1 shows better agreement for the case of pure water).

RESULTS AND DISCUSSIONS

Figure-3 shows the predicted methane solubility in the water-rich phase in a wide temperature range (i.e., 275 to 400 K), at different isobars. This figure indicates that methane solubility passes through a minimum. The dashed lines show the methane solubility in metastable conditions. Also in the above figure, the concentration of methane in the water-rich phase at water-hydrate and water-hydrate-methane phase equilibria are presented.

For simplicity, the sea water in subsea sediments is represented by 3.5 Wt% NaCl aqueous solution. Methane solubility in the water-rich phase in the presence of sea water, is depicted in Figure-4. Constant pressure lines are replaced by depth, taking into account the density of the sea water. Again the dashed lines, which are the extension of methane solubility in water-gas equilibria, show the methane solubility in the water-rich phase at metastable conditions. For simplicity, pressure (or depth) is assumed to be constant; by cooling and moving along the constant pressure line, the system will approach the water-hydrate-methane equilibrium point, i.e. the potential hydrate formation temperature. Assuming no subcooling is required, methane hydrates could form at this point. In the absence of a free gas phase, a further reduction in temperature will cause more hydrates to form and the methane concentration in equilibrium with hydrates to reduce. Nevertheless, for hydrate formation, a certain degree of subcooling is required. Therefore, the methane concentration in the water rich phase could be as high as those presented by the dash lines. However, when hydrate formation is initiated the equilibrium methane concentration in the water-rich phase is much lower. This means that gas hydrates could form without the presence of a free gas phase.

In the presence of a free gas phase and under the above conditions (constant pressure, temperature, and composition), hydrate formation would cease only when one of the phases (i.e., water or the free gas phase) disappears. However, in the presence of sea water the increase in the concentration of salts (due to hydrate formation) could inhibit the further formation of hydrates, as discussed later.

The effect of salt(s) on the equilibrium concentration of methane in the water-rich phase is presented in Figure-5. As shown, the presence of salt(s) will reduce the methane solubility, and inhibit hydrate formation, as the hydrate-water-methane point for 3.5 Wt% NaCl solution is at a lower temperature compared to pure water.

Figure-6a shows the mole% hydrates formed from dissolved gas in 3.5 Wt% NaCl solution at 280 K. The x-axis is pressure (or depth). As an example, at 20 MPa (1993 m depth), the dissolved gas in the metastable condition is enough to form 1% hydrates. However, the amount of hydrates could be as high as 2.2% for 60 MPa pressure (5980 m depth).

As shown in Figure-6b, the 1% hydrates will increase the salt concentration by 0.03 Wt%, i.e., the salt concentration will increase from 3.5 to 3.53 Wt%. However, the effect on phase equilibria conditions is insignificant (an inhibition of 0.013 K). This means that for further hydrate formation, the controlling factor is

most likely to be the supply of gas. As the gas concentration in the hydrate stability zone is significantly lower, the gas could be transported by diffusion. Convection is also another means of supplying gas to the hydrate stability zone.

Based on the above results the following two mechanisms are proposed for hydrate formation in subsea sediments:

1. Hydrate formation from dissolved gas:

- Gas released from biogenic and thermogenic sources are dissolved in sea water.
- The dissolved gas reaches the hydrate stability zone by diffusion, or the water containing the dissolved gas reaches the hydrate stability zone by convection/advection.
- Hydrate formation initiates at a certain degree of subcooling and the concentration of gas in the water-rich phase is reduced, as shown in Figure-4. Therefore, the gas concentration (in the water-rich phase) outside the hydrate stability zone would be higher than that inside the hydrate stability zone.
- More gas is provided to the hydrate stability zone by diffusion (due to the concentration gradient) for further hydrate formation.

As mentioned previously, the increase in salt concentration due to hydrate formation is very small. Therefore, the diffusion of gas from the high concentration region to the hydrate stability zone is likely to be the controlling factor.

2. Hydrate formation from free gas:

- Free gas is generated in-situ, or reaches the hydrate stability zone by convection.
- Large amounts of hydrates could be formed which could result in the consumption of all the free gas, or a significant increase in the salt concentration in the pores.
- The increase in salt concentration could inhibit further hydrate formation (Figure-5), unless the salt concentration is reduced by diffusion.
- More free gas is converted into hydrates. This process will terminate when all the gas (or water) is converted into hydrates.

In the above mechanism, the transfer of salts by diffusion is likely to be the controlling factor.

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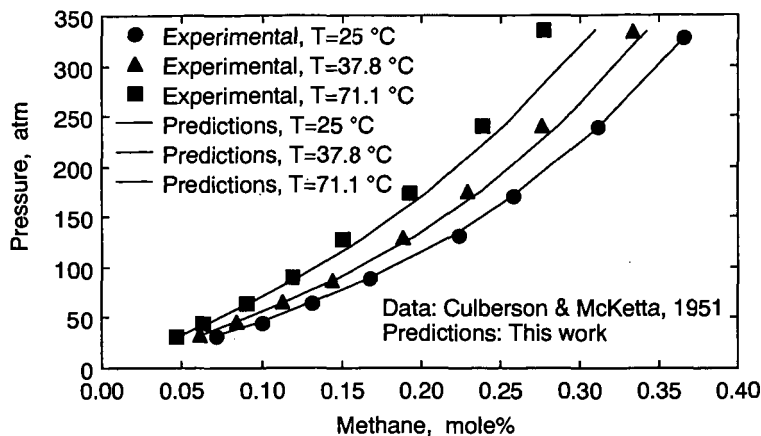


Figure-1 Experimental and predicted methane solubilities in distilled water.

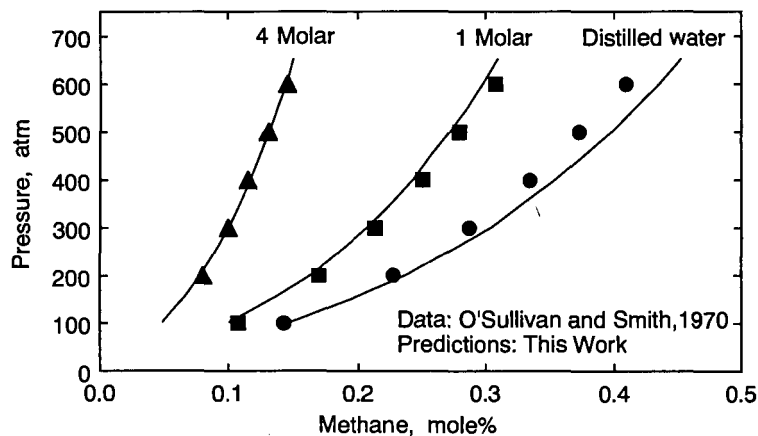


Figure-2 Experimental and predicted methane solubilities in distilled water and NaCl aqueous solutions.

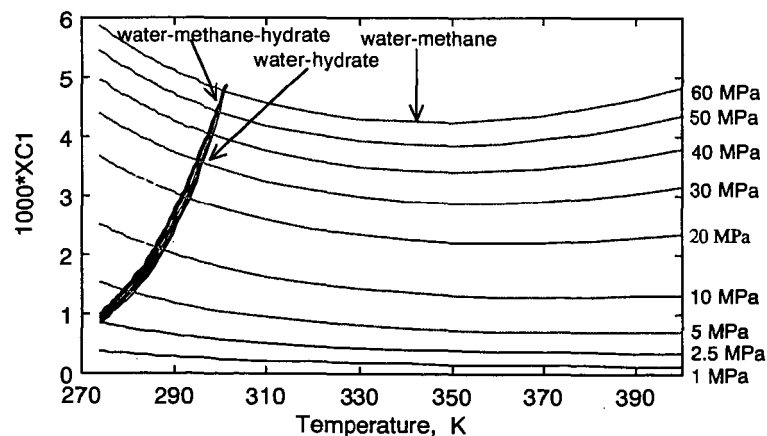


Figure-3 Predicted methane concentrations in the water-rich phases (Salt free) of water-methane, water-methane-hydrate, and water-hydrate equilibria.

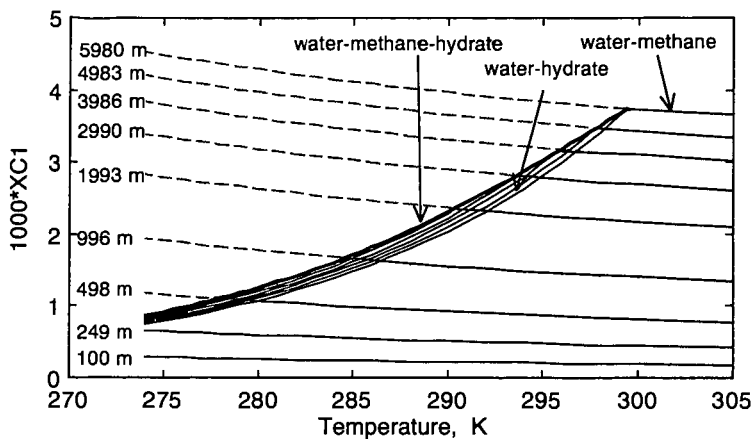


Figure-4 Predicted methane concentrations in the water-rich phases (3.5 Wt% NaCl) of water-methane, water-methane-hydrate, and water-hydrate equilibria.

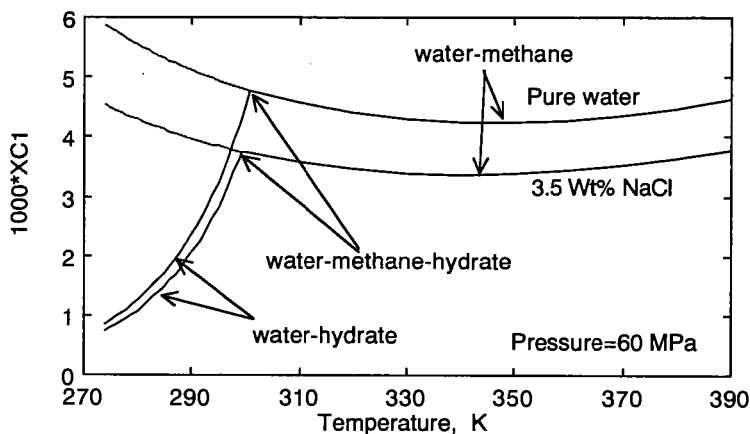


Figure-5 Effect of water salinity on methane concentration.

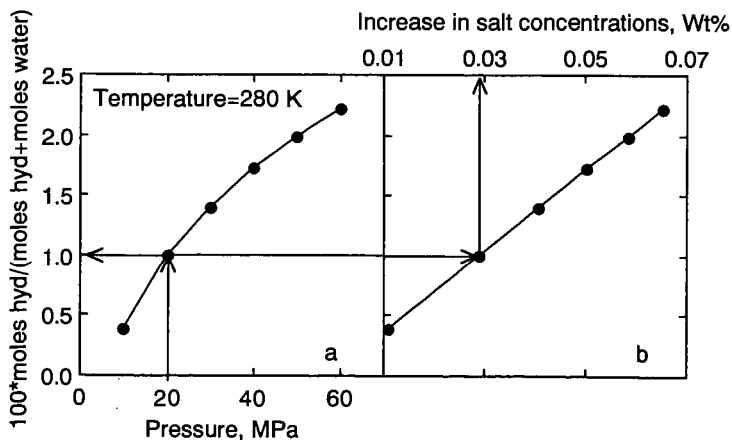


Figure-6 Percent hydrates formed from the dissolved methane and the increase in salt concentration.